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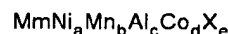
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(54) HYDROGEN-OCCLUDING ALLOY AND PROCESS FOR PRODUCING THE SAME

(57) A hydrogen storage material which is an AB₅ type hydrogen storage alloy having a CaCu₅ type crystal structure represented by general formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$,
 $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and
 $5.2 \leq a+b+c+d \leq 5.45$,
or general formula:



wherein Mm is a misch metal, X is Cu and/or Fe,
 $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$,
and $5.2 \leq a+b+c+d+e \leq 5.45$,
characterized in that the lattice length on the c-axis is
406.2 pm or more, and a process of producing the same.

Description**Technical Field:**

[0001] The present invention relates to a hydrogen storage material and a process of producing the same. More particularly, it relates to a hydrogen storage material which is, while with a minimized cobalt content, excellent in insusceptibility to grain size reduction and hydrogen storage characteristics (PCT characteristics) and exhibits not only excellent initial activity that is an important characteristic for use in a battery but high output characteristics for use in electric tools, etc. or low-temperature characteristics for use in hybrid electric vehicles, and a process for producing the same.

Background Art:

[0002] Nickel-metal hydride storage batteries (secondary batteries) having a hydrogen storage material in the anode have recently been attracting attention as high capacity alkali storage batteries supplanting nickel-cadmium storage batteries. The hydrogen storage materials that are currently used widely are hydrogen storage alloys composed of five elements, i.e., Mm (misch metal, a mixture of rare earth elements), Ni, Al, Mn, and Co.

[0003] Compared with La-based alloys, the Mm-Ni-Mn-Al-Co alloys enable constructing an anode out of relatively cheap materials and provide closed nickel-metal hydride storage batteries having a long cycle life and a controlled inner pressure rise which is caused by gas generated in case of an overcharge and have therefore been used widely as an electrode material.

[0004] The Mm-Ni-Mn-Al-Co alloys in current use are designed to have a prolonged cycle life by preventing the alloys from reducing their grain size. It is generally known that about 10% by weight of Co (0.6 to 1.0 in an atomic ratio) is required to prevent the grain size reduction. It is also accepted that a given amount of Co is necessary for securing excellent hydrogen storage characteristics and anticorrosion.

[0005] However, the material cost increases with the Co content, which is problematical from the aspect of material cost. Taking into consideration application of the hydrogen storage material to large batteries, such as the power source of electric vehicles, and the ever expanding market of nickel-metal hydride storage batteries, in particular, the material cost is weighty in choosing anode materials and has been a matter of concern.

[0006] To settle the above problem, JP-A-9-213319 proposes altering the composition of the Mm-Ni-Mn-Al-Co alloy and adding thereto a small amount of an additional element. Use of the hydrogen storage material powder disclosed therein as an anode makes it feasible to reduce the Co content and yet to suppress deterioration of the anode caused by the alloy's reduction in grain size below a certain level and thereby to extend the cycle life of the battery.

[0007] Because the alloy of the composition disclosed in JP-A-9-323319 does not always secure stability in its characteristics, the present inventors have proposed in JP-A-11-152533 a composition and a production process for obtaining satisfactory initial activity, whereby a low-Co alloy has now come to be used in special applications.

[0008] However, where the hydrogen storage materials disclosed in the above publications (JP-A-9-213319 and JP-A-11-152533) are used, output characteristics, especially output in low temperature, are insufficient for electric tools needing high output characteristics or for hybrid electric vehicles.

[0009] Accordingly, an object of the present invention is to provide a hydrogen storage material of which the production cost is reduced by extremely decreasing its cobalt content and which exhibits excellent insusceptibility to grain size reduction, excellent hydrogen storage characteristics, satisfactory output characteristics, and satisfactory storage characteristics and a process for producing the same.

Disclosure of the Invention:

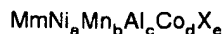
[0010] As a result of extensive studies, the present inventors have found that the above object is accomplished by a hydrogen storage material of AB_5 structure having a specific stoichiometric composition (B site rich), particularly a composition having $4.1 < Ni \leq 4.3$ and $0.4 < Mn \leq 0.6$, and the c-axis of which is in a given range. They have also found that such a hydrogen storage material is obtainable with the above-described specific composition when a casting temperature and heat treating conditions satisfy a given relationship.

[0011] The present invention has been reached based on the above findings and provides a hydrogen storage material which is an AB_5 type hydrogen storage alloy having a $CaCu_5$ type crystal structure represented by general formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and $5.2 \leq a+b+c+d \leq 5.45$.

or general formula:



wherein Mm is a misch metal, X is Cu and/or Fe, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$, and $5.2 \leq a+b+c+d+e \leq 5.45$,

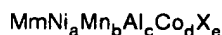
characterized in that the lattice length on the c-axis is 406.2 pm or more.

[0012] The present invention also provides a preferred process for producing the hydrogen storage material of the present invention which comprises heat-melting hydrogen storage alloy raw materials, casting the melt, and heat treating the resulting alloy in an inert gas atmosphere to produce an AB₅ type hydrogen storage material having a CaCu₅ type crystal structure represented by the following general formulae, characterized in that the casting temperature is 1350 to 1550°C, the pouring temperature is 1200 to 1450°C, and conditions of said heat treating are 1040 to 1080°C and 1 to 6 hours.

General formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and $5.2 \leq a+b+c+d \leq 5.45$, or general formula:



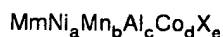
wherein Mm is a misch metal, X is Cu and/or Fe, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$, and $5.2 \leq a+b+c+d+e \leq 5.45$.

The Best Mode for Carrying out the Invention:

[0013] The hydrogen storage material according to the present invention is an AB₅ type hydrogen storage alloy having a CaCu₅ type crystal structure represented by general formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and $5.2 \leq a+b+c+d \leq 5.45$, or general formula:



wherein Mm is a misch metal, X is Cu and/or Fe, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$, and $5.2 \leq a+b+c+d+e \leq 5.45$.

[0014] In the above formulae, Mm is a misch metal, a mixture of rare earth elements such as La, Ce, Pr, Nd, and Sm. The hydrogen storage material is an AB₅ type hydrogen storage alloy having a CaCu₅ type crystal structure having a B site-rich nonstoichiometric composition ranging from AB_{5.2} to AB_{5.45}.

[0015] In this hydrogen storage material, the compositional ratio (atomic ratio) of Ni_aMn_bAl_cCo_d fulfills the following relationships. The ratio of Ni: $4.1 < a \leq 4.3$. The ratio of Mn: $0.4 < b \leq 0.6$. The ratio of Al: $0.2 \leq c \leq 0.4$. The ratio of Co: $0.1 \leq d \leq 0.4$. (a+b+c+d) is in a range of from 5.2 to 5.45.

[0016] The compositional ratio (atomic ratio) of Ni_aMn_bAl_cCo_dX_e (wherein X is Cu and/or Fe) satisfies the following relationships. The ratio of Ni: $4.1 < a \leq 4.3$. The ratio of Mn: $0.4 < b \leq 0.6$. The ratio of Al: $0.2 \leq c \leq 0.4$. The ratio of Co: $0.1 \leq d \leq 0.4$. The ratio of X: $0 < e \leq 0.1$. (a+b+c+d+e) is in a range of from 5.2 to 5.45.

[0017] As described above, the ratio of Ni, \underline{a} , is more than 4.1 and up to 4.3, desirably from 4.15 to 4.25. If \underline{a} is 4.1 or less, the output characteristics are not satisfactory. If it exceeds 4.3, deterioration in insusceptibility to grain size reduction or life characteristics is observed.

[0018] The ratio of Mn, \underline{b} , is more than 0.4 and up to 0.6. If \underline{b} is 0.4 or less, the plateau pressure increases, and the hydrogen storage capacity is reduced. If it exceeds 0.6, the alloy undergoes considerable corrosion so that the battery

voltage greatly decreases during storage.

[0019] The ratio of Al, c, is from 0.2 to 0.4. If c is smaller than 0.2, the plateau pressure, which is the hydrogen release pressure of a hydrogen storage material, increases to deteriorate energy efficiency in charges and discharges. If it exceeds 0.4, the hydrogen storage capacity is reduced.

[0020] The ratio of Co, d, is 0.1 to 0.4. If d is less than 0.1, the hydrogen storage characteristics or the resistance to grain size reduction are deteriorated. If it exceeds 0.4, the proportion of Co increases, failing to realize cost reduction.

[0021] The ratio of X, e, is from 0 to 0.1. If e is more than 0.1, the output characteristics are impaired, and the hydrogen storage capacity is reduced.

[0022] $(a+b+c+d)$ or $(a+b+c+d+e)$ (these sums will hereinafter be sometimes referred to as x, inclusively) is from 5.2 to 5.45. If x is smaller than 5.2, the battery life and the resistance to grain size reduction are ruined. If x is greater than 5.45, the hydrogen storage characteristics are reduced and, at the same time, the output characteristics are also deteriorated.

[0023] The hydrogen storage material of the present invention has a lattice length on the c-axis of 406.2 pm or more, preferably 406.6 to 407.1 pm. If the lattice length on the c-axis is shorter than 406.2 pm, the alloy has poor insusceptibility to grain size reduction and reduced battery life characteristics.

[0024] The c-axis lattice length of the hydrogen storage material has different preferred ranges according to the value of $(a+b+c+d)$ or $(a+b+c+d+e)$, i.e., the value x. The value x being 5.02 or greater and smaller than 5.3, the c-axis lattice length is preferably 406.2 to 406.8 pm. The value x ranging from 5.3 to 5.45, the c-axis lattice length is preferably 406.8 to 407.3 pm.

[0025] Although the lattice length on the a-axis of the hydrogen storage material of the present invention is not particularly limited, it is usually from 500.5 to 501.2 pm.

[0026] The process of producing the hydrogen storage material of the present invention is then described. Raw materials of the hydrogen storage material are weighed to give the alloying composition described above and mixed up. The mixture is melted into a melt by means of a high frequency induction furnace based on induction heating. The melt is poured into a casting mold, for example, a mold of water cooling type at a casting temperature of 1350 to 1550°C to obtain a hydrogen storage material. The pouring temperature is 1200 to 1450°C. The term "casting temperature" as used herein means the temperature of the melt in the crucible at the beginning of casting, and the term "pouring temperature" means the temperature of the melt at the inlet of the casting mold (i.e., the temperature of the melt before entering the casting mold).

[0027] The resulting hydrogen storage material is heat treated in an inert gas atmosphere, for example, in argon gas under heat treating conditions of 1040 to 1080°C and 1 to 6 hours. A cast alloy structure usually shows fine grain boundary segregation chiefly of Mn. The heat treatment is to level the segregation by heating.

[0028] There is thus obtained a hydrogen storage material which has a reduced cobalt content and yet exhibits excellent insusceptibility to grain size reduction, excellent hydrogen storage characteristics, satisfactory output characteristics, and satisfactory storage characteristics.

[0029] The hydrogen storage material is crushed, pulverized, and subjected to surface treatment, such as an acid treatment, an alkali treatment or a like treatment and is suitably used as an anode of high-output alkali storage batteries. The alkali storage batteries thus provided are satisfactory in initial characteristics and low-temperature high-output characteristics. The anode made of the hydrogen storage material is prevented from deterioration due to the alloy getting finer and therefore secures a long cycle life.

[0030] The present invention will further be illustrated in the concrete by way of Examples and the like.

Examples 1 to 8, Reference Examples 1 to 2, and Comparative Examples 1 to 4

[0031] Raw materials of a hydrogen storage material were weighed to make the alloying composition shown in Table 1 and mixed up. The mixture was put in a crucible, and the crucible was set in a high frequency melting furnace. After evacuating to a degree of vacuum of 10^{-4} to 10^{-5} Torr, the mixture was heat melted in an argon gas atmosphere and cast into a copper casting mold of water cooling type at 1350°C (pouring temperature: 1250°C) to obtain an alloy. The resulting alloy was heat treated in an argon atmosphere under the conditions shown in Table 2 to obtain a hydrogen storage material. Reference Example 1 shows the characteristics of a conventional alloy having a Co content of 10 wt%, and Reference Examples 1-2 and 1-3 show the characteristics of conventional alloys having a Co content of 5 wt%.

Evaluation of Characteristics:

[0032] The lattice length, PCT capacity, grain size retention, storage anticorrosion, output, and electrode life of the hydrogen storage materials obtained in Examples and Comparative Examples were determined in accordance with the following methods. The results obtained are shown in Table 2.

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Lattice length:

[0033] Measured by powder X-ray diffractometry using CuK α rays.

PCT capacity:

[0034] Calculated from the hydrogen absorption measured at 45°C. H/M: 0 to 0.5 MPa.

Grain Size Retention:

[0035] Hydrogen gas of 30 bar was introduced into the hydrogen storage material having a grain size adjusted to 22 to 53 microns in a PCT apparatus to make the material absorb hydrogen, followed by hydrogen desorption. The hydrogen absorption and desorption were repeated 10 cycles, and the ratio of the average grain size after the cycle test to that before the cycle test was obtained.

Corrosion in storage:

(1) Total corrosion

[0036] A corrosion behavior in storage was evaluated as follows. A classified hydrogen storage material powder was made to absorb hydrogen once for activation by use of a cell for PCT evaluation. The cell was put into an aqueous KOH solution having a specific gravity of 1.30 and left to stand as such at 80°C for 4 hours to conduct a dissolution test. The amount of the precipitate on the surface and the amount of dissolved alloy components were determined to give a total corrosion. The total corrosion was relatively expressed in terms of an index based on that of Reference Example 1 taken as 100.

(2) VSM (vibration sample magnetometer) value

[0037] After the determination of the total corrosion, the magnetization of the alloy attributed to Ni and Co on the alloy powder surface was measured with a VSM, which was evaluated as an indication of the degree of corrosion.

Preparation of electrode cell:

[0038] A powdered hydrogen storage material having a grain size adjusted to 22 to 53 microns was mixed with prescribed amounts of a conductive agent and a binder. The mixed powder was pressed into a pellet electrode, which was used as an anode. The pellet anode was combined with a cathode having a sufficient capacity (sintered nickel hydroxide) with a separator interposed therebetween. The combined electrodes were dipped in a KOH aqueous solution having a specific gravity of 1.30 to prepare a model cell.

Setting of charge and discharge conditions:

[0039]

1) For measurement of output characteristics

Charge: 0.2 C - 130%; Discharge: 1 C - 0.7 V (cut-off)
Temperature: 0°C

2) For life test

Charge: 2 C/3-1h; Discharge: 2 C/3-1h
Cycle: 100 cycles

Output:

[0040] After the initial activation, a low-temperature and high-rate discharge capacity (0°C, 1C) was measured under the above-described conditions.

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Electrode life:

[0041] After the above-described life test, the cell was subjected to a charge at 0.2 C - 130% followed by a discharge at 0.2C - 0.7V cut-off to measure the discharge capacity. A ratio of the measured discharge capacity to the initial discharge capacity after the activation was evaluated as a capacity retention.

TABLE 1

	B/A	Mm	Ni	Mn	Al	Co	Fe	Cu
Ref. Example 1	5.0	1	3.55	0.4	0.3	0.75	-	-
Ref. Example 2	5.2	1	4.00	0.4	0.3	0.4	-	0.1
Example 1	5.3	1	4.2	0.5	0.3	0.3	-	-
Example 2	5.25	1.01	4.2	0.5	0.3	0.3	-	-
Example 3	5.20	1.02	4.2	0.5	0.3	0.3	-	-
Example 4	5.35	0.99	4.2	0.5	0.3	0.3	-	-
Example 5	5.41	0.98	4.2	0.5	0.3	0.3	-	-
Comp. Example 1	5.15	1.03	4.2	0.5	0.3	0.3	-	-
Comp. Example 2	5.46	0.97	4.2	0.5	0.3	0.3	-	-
Example 6	5.3	1	4.2	0.5	0.3	0.2	-	0.1
Example 7	5.3	1	4.2	0.5	0.3	0.2	0.1	-
Example 8	5.0	1	4.2	0.6	0.2	0.3	-	-
Comp. Example 3	5.2	1	4.3	0.2	0.4	0.3	-	-
Comp. Example 4	5.0	1	4.1	0.3	0.3	0.3	-	-

TABLE 2

	Heat Treatment (°C/hr)	Lattice Length		PCT Capacity (H/M)	Grain Size Retention (%)	Corrosion in Storage		Output (mAh/g)	Electrode Life (%)
		(a/pm)	(c/pm)			VSM	Total		
Ref. Example 1	1060-3	499.1	406.3	0.82	92	3.22	100	220	97
Ref. Example 2-1	1060-3	500.9	406.3	0.82	92	2.21	130	180	96.5
Ref. Example 2-2	1080-3	500.9	406.4	0.82	93	2.10	120	170	97
Example 1-1	1040-3	501.1	406.5	0.82	95	1.90	85	210	98
Example 1-2	1060-3	500.9	406.7	0.81	96	1.50	65	220	99
Example 1-3	1080-3	500.9	406.6	0.81	98	1.73	78	215	97.5

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TABLE 2 (continued)

	Heat Treatment (°C/hr)	Lattice Length		PCT Capacity (H/M)	Grain Size Retention (%)	Corrosion in Storage		Output (mAh/g)	Electrode Life (%)
		(a/pm)	(c/pm)			VSM	Total		
Comp. Example 1-1	1020-3	501.3	406.0	0.83	77	2.35	145	220	87
Comp. Example 1-2	1100-3	501.2	406.1	0.83	83	2.20	120	190	88
Example 2	1060-3	501.3	406.5	0.83	95	2.00	95	215	97
Example 3	1060-3	501.5	406.4	0.85	93	2.10	100	225	96.5
Example 4	1060-3	500.6	406.9	0.80	99	1.45	60	175	99
Example 5	1060-3	500.5	407.0	0.79	99	1.40	50	170	98
Example 6	1060-3	500.9	406.6	0.81	97	1.75	90	210	97
Example 7	1060-3	500.7	406.8	0.80	98	2.05	100	195	98
Example 8	1060-3	501.2	406.8	0.83	94	2.05	95	225	97
Comp. Example 3	1060-3	500.5	407.3	0.75	94	2.74	140	120	94
Comp. Example 4	1060-3	500.7	404.9	0.83	65	2.95	160	190	89

[0042] As is apparent from the results in Table 2, Examples show higher levels of grain size retention, battery output and electrode life in good balance than Comparative Examples. It is also understood that Examples have a lower magnetization and a less total corrosion than Comparative Examples, being proved superior in storage characteristics and life as a battery. Further, Examples are generally equal to Reference Examples in terms of PCT capacity, battery output and electrode life and superior in grain size retention and anticorrosion during storage.

Industrial Applicability:

[0043] The hydrogen storage material of the present invention has an extremely reduced cobalt content and therefore enjoys a reduction in production cost. It is excellent in resistance against grain size reduction and hydrogen storage characteristics and satisfactory in output characteristics and storage characteristics.

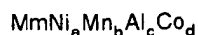
[0044] The production process according to the present invention provides the above-described hydrogen storage material stably and efficiently.

Claims

1. A hydrogen storage material which is an AB₅ type hydrogen storage alloy having a CaCu₅ type crystal structure

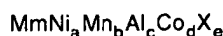
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represented by general formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and $5.2 \leq a+b+c+d \leq 5.45$,
characterized in that the lattice length on the c-axis is 406.2 pm or more.

2. A hydrogen storage material which is an AB_5 type hydrogen storage alloy having a CaCu_5 type crystal structure represented by general formula:



wherein Mm is a misch metal, X is Cu and/or Fe, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$, and $5.2 \leq a+b+c+d+e \leq 5.45$,
characterized in that the lattice length on the c-axis is 406.2 pm or more.

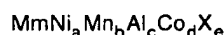
3. The hydrogen storage material according to claim 1 or 2, wherein said lattice length on the c-axis is from 406.6 to 407.1 pm.
4. The hydrogen storage material according to claim 1 or 2, wherein $(a+b+c+d)$ or $(a+b+c+d+e)$ is 5.2 or greater and smaller than 5.3, and said lattice length on the c-axis is 406.2 or greater and smaller than 406.8 pm.
5. The hydrogen storage material according to claim 1 or 2, wherein $(a+b+c+d)$ or $(a+b+c+d+e)$ is from 5.3 to 5.45, and said lattice length on the c-axis is from 406.8 to 407.3 pm.

6. A process for producing a hydrogen storage material comprising heat-melting raw materials of a hydrogen storage material, casting the melt, and heat treating the cast product in an inert gas atmosphere to produce an AB_5 type hydrogen storage material having a CaCu_5 type crystal structure represented by the following general formulae,
characterized in that the casting temperature is 1300 to 1550°C, the pouring temperature is 1200 to 1450°C, and conditions of said heat treating are 1040 to 1080°C and 1 to 6 hours.
 General formula:



wherein Mm is a misch metal, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, and $5.2 \leq a+b+c+d \leq 5.45$.

7. A process for producing a hydrogen storage material comprising heat-melting raw materials of a hydrogen storage material, casting the melt, and heat treating the cast product in an inert gas atmosphere to produce an AB_5 type hydrogen storage material having a CaCu_5 type crystal structure represented by the following general formulae,
characterized in that the casting temperature is 1300 to 1550°C, the pouring temperature is 1200 to 1450°C, and conditions of said heat treating are 1040 to 1080°C and 1 to 6 hours.
 General formula:



wherein Mm is a misch metal, X is Cu and/or Fe, $4.1 < a \leq 4.3$, $0.4 < b \leq 0.6$, $0.2 \leq c \leq 0.4$, $0.1 \leq d \leq 0.4$, $0 < e \leq 0.1$, and $5.2 \leq a+b+c+d+e \leq 5.45$.

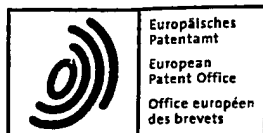
INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/03830

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C 1/00, 19/00, C22F 1/02, B22D 7/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C22C 1/00-1/02, 19/00-19/03, C22F 1/00-1/02, B22D 7/00, H01M 4/38		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-310838 A (Mitsui Mining & Smelting Co., Ltd.), 09 November, 1999 (09.11.99), Claims 1 to 4; Par. Nos. 0025 to 0027 (Family: none)	2-5,7 1-7
Y	JP 11-354116 A (Japan Metals & Chemicals Co., Ltd.), 24 December, 1999 (24.12.99), Claim 3 (Family: none)	1-7
Y	JP 2000-12012 A (Sanyo Electric Co., Ltd.), 14 January, 2000 (14.01.00), Claim 1 (Family: none)	1-7
Y	JP 11-152533 A (Mitsui Mining & Smelting Co., Ltd.), 08 June, 1999 (08.06.99), Claims 1 to 7 (Family: none)	1-7
P,X	JP 2000-219928 A (Mitsui Mining & Smelting Co., Ltd.), 08 August, 2000 (08.08.00), Claims 1 to 5; working example (Family: none)	2-5,7
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 31 July, 2001 (31.07.01)		Date of mailing of the international search report 14 August, 2001 (14.08.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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Applicant/Proprietor MITSUI MINING & SMELTING CO., LTD.	

Communication

The European Patent Office herewith transmits as an enclosure the supplementary European search report under Article 153(7) EPC for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

- ☒ Additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

Refund of the search fee

If applicable under Article 9 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 227 165 A (MITSUI MINING & SMELTING CO [JP]) 31 July 2002 (2002-07-31) * the whole document *	1-10, 12	INV. C22C19/00 H01M4/38 C07H21/00 G01N33/53
A	JP 2002 212601 A (MITSUI MINING & SMELTING CO) 31 July 2002 (2002-07-31) * the whole document *	1-10, 12	
A	WO 03/056047 A (SANTOKU CORP [JP]; TAKAMARU KIYOFUMI [JP]; HAYASHI HIROKI [JP]; IKEDA) 10 July 2003 (2003-07-10) * the whole document *	1-10, 12	
A	WO 03/054240 A (SANTOKU CORP [JP]; TAKAMARU KIYOFUMI [JP]; HAYASHI HIROKI [JP]; IKEDA) 3 July 2003 (2003-07-03) * the whole document *	1-10, 12	
A, P	EP 1 386 974 A (SANTOKU CORP [JP]) 4 February 2004 (2004-02-04) * the whole document *	1-10, 12	TECHNICAL FIELDS SEARCHED (IPC) C22C C07H G01N
The supplementary search report has been based on the last set of claims valid and available at the start of the search.			
Place of search Munich		Date of completion of the search 15 May 2008	Examiner von Zitzewitz, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:
- ☒ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-10, 12

This invention relates to the problem of adapting the total of Ni, Mn, Al and Co ($a+b+c+d$) and the length of the a- and c-axis to each other.

The STF, which is not known from D1, relating to this problem is the combination of specific " $a+b+c+d$ " values and specific a-axis and c-axis lengths as defined e.g. in claim 4.

2. claim: 11

This invention relates to the problem of obtaining a specific pulverization residual rate.

The STF, which is not known from D1, is a pulverization residual rate 50% defined in claim 11.

1.1 According to Article 82 EPC and Rule 44 EPC, an application must relate to one invention only or to a group of inventions so linked as to form a "Single General Inventive Concept" (SGIC; not known from the prior art): unity of invention.

Unity of invention is fulfilled only when there is a technical relationship among the inventions involving at least one identical or corresponding special technical feature (STF; this feature defines the contribution over the prior art).

1.2 The single general concept, which is common to claims 4 and 11 is a hydrogen storage alloy having a CaCu_5 type crystal structure with the formula $\text{MmNi}_a\text{Mn}_b\text{Al}_c\text{Co}_d$ and having specific a-axis and c-axis lengths. The features of this concept are defined in claim 1.

1.3 Examples 1 and 8 of D1 (EP 1 227 165 A1; paragraph 41, tables 1 and 2), which is considered to be the closest prior art, disclose a hydrogen storage alloy having a CaCu_5 type crystal structure (D1, claim 1) with the formula $\text{MmNi}_a\text{Mn}_b\text{Al}_c\text{Co}_d\text{Fe}_e$, wherein:

- Mm is a Misch metal
- $a = 4.2$
- $0.5 \leq b \leq 0.6$
- $0.2 \leq c \leq 0.3$
- $d = 0.3$
- $a+b+c+d+e = 5.30$
- 500.6 a-axis length of the crystal lattice 501.5
- 406.4 c-axis length of the crystal lattice 406.9.

Therefore, the subject-matter of claim 1 and consequently the described single general concept is known from D1.

1.4 Consequently, the following different inventions are claimed:



The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

I.) Claims 1-10 and 12:

This invention relates to the problem of adapting the total of Ni, Mn, Al and Co ($a+b+c+d$) and the length of the a- and c-axis to each other. The STF, which is not known from D1, relating to this problem is the combination of specific " $a+b+c+d$ " values and specific a-axis and c-axis lengths as defined e.g. in claim 4.

II.) Claim 11:

This invention relates to the problem of obtaining a specific pulverization residual rate. The STF, which is not known from D1, is a pulverization residual rate 50% defined in claim 11.

1.5 These inventions manifestly relate to different problems, which are not related to each other. In summary, the inventions are not linked so as to form a SGIC and have no corresponding STF. Consequently, the application as filed lacks unity, wherefore a partial search report has been drafted for invention I.) only.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 77 1377

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-05-2008

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